

UNITED STATES PATENT AND TRADEMARK OFFICE

Examiner: Group: Attorney Docket # 1931

Applicant(s) : CHASSOT, L., ET AL

Serial No. :

Filed :

For : DYES FOR KERATIN FIBERS, THE DYES
CONTAINING N-BENZYL-P-PHENYLENEDIAMINE
DERIVATIVES, AND NOVEL N-BENZYL-P-
PHENYLENEDIAMINE DERIVATIVES

SIMULTANEOUS AMENDMENT

February 1, 2002

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

S I R S:

Simultaneously with filing of the above identified application
please amend the same as follows:

In the Claims:

Cancel all claims without prejudice.

Substitute the claims attached hereto.

REMARKS:

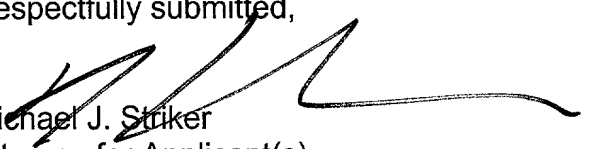
This Amendment is submitted simultaneously with filing of the above identified
application.

With the present Amendment applicant has amended the claims so as to eliminate
their multiple dependency.

10/049667-010102

Consideration and allowance of the present application is most respectfully requested.

Respectfully submitted,

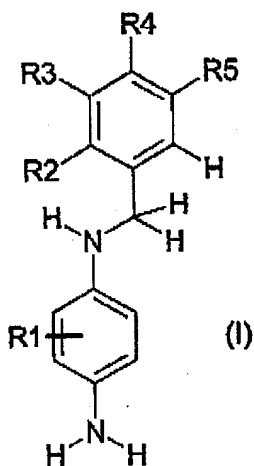


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Claims

1. N-benzyl-p-phenylenediamine derivatives of the general Formula (I) or their physiologically compatible, water-soluble salts



in which

- R1 is hydrogen, a (C₁-C₄) alkyl group or a hydroxy-(C₁-C₄) alkyl group,
- R2 is hydrogen, a halogen atom (F, Cl, Br, I), a cyano group, a (C₁-C₄) alkoxy group, a hydroxy (C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, a nitro group, an amino group, a (C₁-C₄) alkylamino group, a di-(C₁-C₄) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a (hydroxy-(C₁-C₄)-alkyl) amino group, a trifluoromethane group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group, a dihydroxy-(C₃-C₄) alkyl group or a morpholino group
- R3, R4 independently of one another are hydrogen, a halogen atom, a hydroxy group, a (C₁-C₄) alkoxy group, a hydroxy-(C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, an amino group, a (C₁-C₆) alkylamino group, a di-(C₁-C₆) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl)amino group, a hydroxy-(C₁-C₄)

alkylamino group, a trifluoromethane group, an acetamido group, a $-\text{C}(\text{O})\text{CH}_3$ group, a $-\text{C}(\text{O})\text{CF}_3$ group, an $-\text{Si}(\text{CH}_3)_3$ group, a hydroxy- $(\text{C}_1\text{-C}_4)$ alkyl group or a dihydroxy- $(\text{C}_3\text{-C}_4)$ alkyl group or R3 and R4 together form an $-\text{O}-\text{CH}_2-\text{O}-$ bridge and

R5 is hydrogen, a hydroxy group or a $(\text{C}_1\text{-C}_6)$ alkyl group,

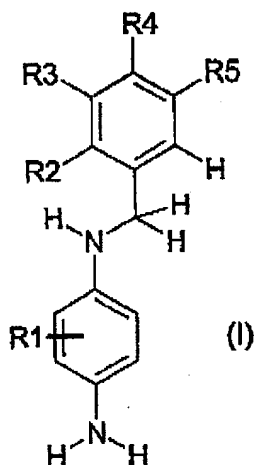
with the proviso that

- (i) at least one of the R2 to R5 groups is different from a hydrogen and
- (ii) R1 is not hydrogen or a $(\text{C}_1\text{-C}_4)$ alkyl group when $\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{hydrogen}$ and $\text{R}_3 = \text{chlorine}$ and
- ((iii) R4 is not a nitro group, a methyl group, a hydroxy group, an amino group, a dimethylamino group, a bromine atom or a chlorine atom when $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_5 = \text{hydrogen}$.

2. Compounds of Formula (I) are preferred in which

- (i) R1 and one of the groups R2 to R5 is hydrogen and/or
- (ii) three of the R1 to R5 groups are hydrogen and the two remaining groups, independently of one another, represent hydrogen, a methoxy group, a hydroxy group or an amino group or, in the case of R3 and R4, jointly form an $-\text{O}-\text{CH}_2-\text{O}$ bridge, in which case R2 is not a hydroxy group and at least one of the R2 to R5 groups is not hydrogen; and/or
- (iii) four of the R1 to R5 groups are hydrogen and the fifth group is a methoxy group, a hydroxyethoxy group, a hydroxy group or an amino group, R2 not being a hydroxy group and at least one of the R2 to R5 groups being different from hydrogen.

3. An agent for dyeing keratin fibers based on a combination of developer and coupler, wherein, as developer, at least one N-benzyl-p-phenylenediamine derivative of Formula (I) or its physiologically compatible, water soluble salt is contained



in which

R1 is hydrogen, a (C₁-C₄) alkyl group or a hydroxy-(C₁-C₄) alkyl group

R2 is hydrogen, a halogen atom (F, Cl, Br, I), a cyano group, a (C₁-C₄) alkoxy group, a hydroxy (C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, a nitro group, an amino group, a (C₁-C₄) alkylamino group, a di-(C₁-C₄) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a (hydroxy-(C₁-C₄)-alkyl) amino group, a trifluoromethane group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group, a dihydroxy-(C₃-C₄) alkyl group or a morpholino group

R3, R4 independently of one another are hydrogen, a halogen atom, a hydroxy group, a (C₁-C₄) alkoxy group, a hydroxy-(C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, an amino group, a (C₁-C₆) alkylamino group, a di-(C₁-C₆) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a hydroxy-(C₁-C₄) alkylamino group, a trifluoromethane group, an acetamido group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group or a dihydroxy-(C₃-C₄) alkyl group or R3 and R4 together form an -O-CH₂-O- bridge and

R5 is hydrogen, a hydroxy group or a (C₁-C₆) alkyl group,

with the proviso that

- (i) at least one of the R2 to R5 groups is different from a hydrogen and
- (ii) R1 is not hydrogen or a (C1-C4) alkyl group when R2 = R4 = R5 = hydrogen and R3 = chlorine.

4. The agent of claim 3, wherein

- (i) R1 and one of the groups R2 to R5 is hydrogen and/or
- (ii) three of the R1 to R5 groups are hydrogen and the two remaining groups, independently of one another, represent hydrogen, or methoxy group, a hydroxy group or an amino group or, in the case of R3 and R4, jointly form an -O-CH₂-O bridge, in which case R2 is not a hydroxy group and at least one of the R2 to R5 groups is not hydrogen; and/or
- (iii) four of the R1 to R5 groups are hydrogen and the fifth group is a methoxy group, a hydroxyethoxy group, a hydroxy group or an amino group, R2 not being a hydroxy group and at least one of the R2 to R5 groups being different from hydrogen, with the proviso that at least one of the R2 to R5 groups is different from hydrogen.

5. The agent of [claims 3 or 4] claim 3, wherein the compound of Formula (I) is selected from the group comprising : N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene; N-((4-aminophenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxyphenyl)-methyl)-1,4-diaminobenzene; N-((2-methoxyphenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxy-3,5-dimethyl-phenyl)methyl)-1,4-diaminobenzene; N-((4-(2-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene; N-benzo[1,3]dioxol-5-ylmethyl-1,4-diaminobenzene; N-{4-[(4-aminophenylamino)-methyl]-phenyl}-acetamide and N-((4-methoxyphenyl)-methyl)-1,4-diaminobenzene, as well as their physiologically compatible salts.

6. The agent of [one of the claims 3 to 5] claim 3, wherein the N-benzyl-p-phenylenediamine derivative of Formula (I) is contained in an amount of 0.005 to 20 percent by weight.

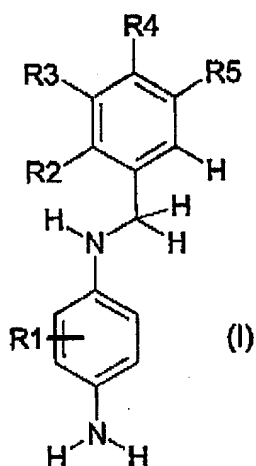
7. The agent of [one of the claims 3 to 6] claim 3, wherein the agent has a pH of 6.5 to 11.5.

8. The agent of [one of the claims 3 to 7] claim 3, wherein the coupler is selected from the group comprising 2,6-diaminopyridine, 2-amino-4-[(2-hydroxyethyl)amino]-anisole, 2,4-diamino-1-fluoro-5-methylbenzene, 2,4-diamino-1-methoxy-5-methylbenzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methylbenzene, 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxybenzene, 2,3-diamino-6-methoxy-pyridine, 3-amino-6-methoxy-2-(methylamino)-pyridine, 2,6-diamino-3,5-dimethoxy-pyridine, 3,5-diamino-2,6-dimethoxy-pyridine, 1,3-diaminobenzene, 2,4-diamino-1-(2-hydroxyethoxy)-benzene, 2,4-diamino-1,5-di(2-hydroxyethoxy)-benzene, 1-(2-aminoethoxy)-2,4-diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methylaminobenzene, 2,4-diaminophenoxyacetic acid, 3-[di(2-hydroxyethyl)amino]-aniline, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene, 5-methyl-2-(1-methylethyl)-phenol, 3-[(2-hydroxyethyl)amino]-aniline, 3-[(2-aminoethyl)-amino]-aniline, 1,3-di(2,4-diaminophenoxy)-propane, di(2,4-diaminophenoxy)-methane, 1,3-diamino-2,4-dimethoxybenzene, 2,6-bis(2-hydroxyethyl)amino toluene, 4-hydroxyindole, 3-dimethylaminophenol, 3-diethylaminophenol, 5-amino-2-methylphenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichlorophenol, 5-amino-2,4-dichlorophenol, 3-amino-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-aminophenol, 2-[(3-hydroxyphenyl)amino]-acetamide, 5-[(2-hydroxyethyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-phenol, 3-[(2-methoxyethyl)-amino]-phenol, 5-amino-2-ethylphenol, 2-(4-amino-2-hydroxyphenoxy)-ethanol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(2,3-dihydroxypropyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-2-methylphenol, 2-amino-3-hydroxy-pyridine, 5-amino-4-chloro-2-methylphenol, 1-naphthol, 1,5-dihydroxy-naphthalene, 1,7-dihydroxy-naphthalene, 2,3-dihydroxy-naphthalene, 2,7-dihydroxy-naphthalene, 2-methyl-1-

naphthol acetate, 1,3-dihydroxybenzene, 1-chloro-2,4-dihydroxybenzene, 2-chloro-1,3-dihydroxybenzene, 1,2-dichloro-3,5-dihydroxy-4-methylbenzene, 1,5-dichloro-2,4-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 3,4-methylenedioxy-phenol, 3,4-methylenedioxy-aniline, 5-[(2-hydroxyethyl)amino]-1,3-benzodioxol, 6-bromo-1-hydroxy-3,4-methylenedioxy-benzene, 3,4-diamino-benzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)-benzoxazine, 3-methyl-1-phenyl-5-pyrazolone, 5,6-dihydroxy-indole, 5,6-dihydroxy-indoline, 5-hydroxy-indole, 6-hydroxy-indole, 7-hydroxy-indole and 2,3-indolinedione.

Claims

1. N-benzyl-p-phenylenediamine derivatives of the general Formula (I) or their physiologically compatible, water-soluble salts



in which

- R1 is hydrogen, a (C₁-C₄) alkyl group or a hydroxy-(C₁-C₄) alkyl group,
- R2 is hydrogen, a halogen atom (F, Cl, Br, I), a cyano group, a (C₁-C₄) alkoxy group, a hydroxy (C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, a nitro group, an amino group, a (C₁-C₄) alkylamino group, a di-(C₁-C₄) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a (hydroxy-(C₁-C₄)-alkyl) amino group, a trifluoromethane group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group, a dihydroxy-(C₃-C₄) alkyl group or a morpholino group
- R3, R4 independently of one another are hydrogen, a halogen atom, a hydroxy group, a (C₁-C₄) alkoxy group, a hydroxy-(C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, an amino group, a (C₁-C₆) alkylamino group, a di-(C₁-C₆) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl)amino group, a hydroxy-(C₁-C₄)

alkylamino group, a trifluoromethane group, an acetamido group, a $-C(O)CH_3$ group, a $-C(O)CF_3$ group, an $-Si(CH_3)_3$ group, a hydroxy- (C_1-C_4) alkyl group or a dihydroxy- (C_3-C_4) alkyl group or R3 and R4 together form an $-O-CH_2-O-$ bridge and

R5 is hydrogen, a hydroxy group or a (C_1-C_6) alkyl group,

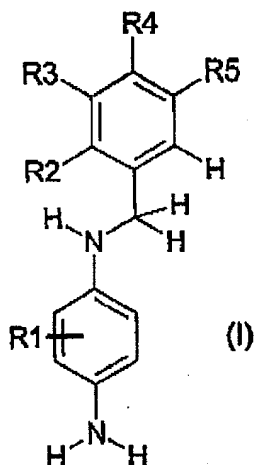
with the proviso that

- (i) at least one of the R2 to R5 groups is different from a hydrogen and
- (ii) R1 is not hydrogen or a (C_1-C_4) alkyl group when $R_2 = R_4 = R_5 = \text{hydrogen}$ and $R_3 = \text{chlorine}$ and
- ((iii) R4 is not a nitro group, a methyl group, a hydroxy group, an amino group, a dimethylamino group, a bromine atom or a chlorine atom when $R_1 = R_2 = R_3 = R_5 = \text{hydrogen}$.

2. Compounds of Formula (I) are preferred in which

- (i) R1 and one of the groups R2 to R5 is hydrogen and/or
- (ii) three of the R1 to R5 groups are hydrogen and the two remaining groups, independently of one another, represent hydrogen, a methoxy group, a hydroxy group or an amino group or, in the case of R3 and R4, jointly form an $-O-CH_2-O$ bridge, in which case R2 is not a hydroxy group and at least one of the R2 to R5 groups is not hydrogen; and/or
- (iii) four of the R1 to R5 groups are hydrogen and the fifth group is a methoxy group, a hydroxyethoxy group, a hydroxy group or an amino group, R2 not being a hydroxy group and at least one of the R2 to R5 groups being different from hydrogen.

3. An agent for dyeing keratin fibers based on a combination of developer and coupler, wherein, as developer, at least one N-benzyl-p-phenylenediamine derivative of Formula (I) or its physiologically compatible, water soluble salt is contained



in which

- R1 is hydrogen, a (C₁-C₄) alkyl group or a hydroxy-(C₁-C₄) alkyl group
- R2 is hydrogen, a halogen atom (F, Cl, Br, I), a cyano group, a (C₁-C₄) alkoxy group, a hydroxy (C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, a nitro group, an amino group, a (C₁-C₄) alkylamino group, a di-(C₁-C₄) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a (hydroxy-(C₁-C₄)-alkyl) amino group, a trifluoromethane group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group, a dihydroxy-(C₃-C₄) alkyl group or a morpholino group
- R3, R4 independently of one another are hydrogen, a halogen atom, a hydroxy group, a (C₁-C₄) alkoxy group, a hydroxy-(C₁-C₄) alkoxy group, a (C₁-C₆) alkyl group, a (C₁-C₄) alkyl thioether group, a mercapto group, an amino group, a (C₁-C₆) alkylamino group, a di-(C₁-C₆) alkylamino group, a di-(hydroxy-(C₁-C₄)-alkyl) amino group, a hydroxy-(C₁-C₄) alkylamino group, a trifluoromethane group, an acetamido group, a -C(O)CH₃ group, a -C(O)CF₃ group, an -Si(CH₃)₃ group, a hydroxy-(C₁-C₄) alkyl group or a dihydroxy-(C₃-C₄) alkyl group or R3 and R4 together form an -O-CH₂-O- bridge and
- R5 is hydrogen, a hydroxy group or a (C₁-C₆) alkyl group,

with the proviso that

- (i) at least one of the R2 to R5 groups is different from a hydrogen and
- (ii) R1 is not hydrogen or a (C1-C4) alkyl group when R2 = R4 = R5 = hydrogen and R3 = chlorine.

4. The agent of claim 3, wherein

- (i) R1 and one of the groups R2 to R5 is hydrogen and/or
- (ii) three of the R1 to R5 groups are hydrogen and the two remaining groups, independently of one another, represent hydrogen, or methoxy group, a hydroxy group or an amino group or, in the case of R3 and R4, jointly form an -O-CH₂-O bridge, in which case R2 is not a hydroxy group and at least one of the R2 to R5 groups is not hydrogen; and/or
- (iii) four of the R1 to R5 groups are hydrogen and the fifth group is a methoxy group, a hydroxyethoxy group, a hydroxy group or an amino group, R2 not being a hydroxy group and at least one of the R2 to R5 groups being different from hydrogen, with the proviso that at least one of the R2 to R5 groups is different from hydrogen.

5. The agent of claim 3, wherein the compound of Formula (I) is selected from the group comprising : N-((3-hydroxyphenyl)methyl)-1,4-diaminobenzene; N-((4-aminophenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxyphenyl)-methyl)-1,4-diaminobenzene; N-((2-methoxyphenyl)methyl)-1,4-diaminobenzene; N-((4-hydroxy-3,5-dimethyl-phenyl)methyl)-1,4-diaminobenzene; N-((4-(2-hydroxyethoxy)-phenyl)methyl)-1,4-diaminobenzene; N-benzo[1,3]dioxol-5-ylmethyl-1,4-diaminobenzene; N-{4-[(4-aminophenylamino)-methyl]-phenyl}-acetamide and N-((4-methoxyphenyl)-methyl)-1,4-diaminobenzene, as well as their physiologically compatible salts.

6. The agent of claim 3, wherein the N-benzyl-p-phenylenediamine derivative of Formula (I) is contained in an amount of 0.005 to 20 percent by weight.

7. The agent of claim 3, wherein the agent has a pH of 6.5 to 11.5.

8. The agent of claim 3, wherein the coupler is selected from the group comprising 2,6-diaminopyridine, 2-amino-4-[(2-hydroxyethyl)amino]-anisole, 2,4-diamino-1-fluoro-5-methylbenzene, 2,4-diamino-1-methoxy-5-methylbenzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methylbenzene, 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxybenzene, 2,3-diamino-6-methoxy-pyridine, 3-amino-6-methoxy-2-(methylamino)-pyridine, 2,6-diamino-3,5-dimethoxy-pyridine, 3,5-diamino-2,6-dimethoxy-pyridine, 1,3-diaminobenzene, 2,4-diamino-1-(2-hydroxyethoxy)-benzene, 2,4-diamino-1,5-di(2-hydroxyethoxy)-benzene, 1-(2-aminoethoxy)-2,4-diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methylaminobenzene, 2,4-diaminophenoxyacetic acid, 3-[di(2-hydroxyethyl)amino]-aniline, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene, 5-methyl-2-(1-methylethyl)-phenol, 3-[(2-hydroxyethyl)amino]-aniline, 3-[(2-aminoethyl)-amino]-aniline, 1,3-di(2,4-diaminophenoxy)-propane, di(2,4-diaminophenoxy)-methane, 1,3-diamino-2,4-dimethoxybenzene, 2,6-bis(2-hydroxyethyl)amino toluene, 4-hydroxyindole, 3-dimethylaminophenol, 3-diethylaminophenol, 5-amino-2-methylphenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichlorophenol, 5-amino-2,4-dichlorophenol, 3-amino-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-aminophenol, 2-[(3-hydroxyphenyl)amino]-acetamide, 5-[(2-hydroxyethyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-phenol, 3-[(2-methoxyethyl)-amino]-phenol, 5-amino-2-ethylphenol, 2-(4-amino-2-hydroxyphenoxy)-ethanol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(2,3-dihydroxypropyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-2-methylphenol, 2-amino-3-hydroxy-pyridine, 5-amino-4-chloro-2-methylphenol, 1-naphthol, 1,5-dihydroxy-naphthalene, 1,7-dihydroxy-naphthalene, 2,3-dihydroxy-naphthalene, 2,7-dihydroxy-naphthalene, 2-methyl-1-naphthol acetate, 1,3-dihydroxybenzene, 1-chloro-2,4-dihydroxybenzene, 2-chloro-1,3-dihydroxybenzene, 1,2-dichloro-3,5-dihydroxy-4-methylbenzene, 1,5-dichloro-2,4-dihydroxybenzene,

1,3-dihydroxy-2-methylbenzene, 3,4-methylenedioxy-phenol, 3,4-methylenedioxy-aniline, 5-[(2-hydroxyethyl)amino]-1,3-benzodioxol, 6-bromo-1-hydroxy-3,4-methylenedioxy-benzene, 3,4-diamino-benzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)-benzoxazine, 3-methyl-1-phenyl-5-pyrazolone, 5,6-dihydroxy-indole, 5,6-dihydroxy-indoline, 5-hydroxy-indole, 6-hydroxy-indole, 7-hydroxy-indole and 2,3-indolinedione.